

CO-CONVERSION OF COAL/WASTE PLASTIC MIXTURES UNDER VARIOUS PYROLYSIS AND LIQUEFACTION CONDITIONS

S.R. Palmer, E.J. Hippo, D. Tandon and M. Blankenship
Department of Mechanical Engineering and Energy Processes,
Southern Illinois University at Carbondale,
Carbondale, Illinois 62901-6603, USA.

Keywords: Copyrolysis, coliquefaction, coal/waste plastic

INTRODUCTION

For strategic and economic reasons the conversion of coal to liquid fuels has been a constant goal of the coal science community (1). Although the economics of coal liquefaction are primarily governed by the price of crude oil, other factors such as the need for large quantities of hydrogen gas, play an important role. If methods could be found that reduce the amount of hydrogen gas required for liquefaction, considerable benefits would be realized. To explore this possibility the use of waste plastics as materials capable of upgrading coal into liquid fuel products has been investigated.

The use of waste plastics for this purpose could become possible because over 30 million tons of synthetic polymer material is produced in the United States every year (2). Some projections estimate that this production will double by the year 2000 (3). The vast majority of this material ends up in the waste stream and is simply landfilled. It is estimated that of the 160 millions tons of municipal solid waste that needs disposal every year in the United States, waste plastics contribute 7-9% by weight and over 20% by volume (4,5). 70% of the discarded plastic is derived from packaging materials of which polyethylene (PE) represents 63%, polypropylene (PP) 9%, polystyrene (PS) 11%, polyvinyl chloride (PVC) 5% and poly(ethylene terephthalate) (PET) 7%.

The concept of using waste plastic to aid the liquefaction of coal is based on the premise that the hydrogen present in many waste plastics can be used to hydrogenate coal. It is believed that this would be possible because waste plastics usually have very high hydrogen contents (14.3 % for PE and PP) compared to most raw coals (5-6%). It is anticipated that coal/waste plastic co-pyrolysis procedures could allow for hydrogen migration from the plastic to the coal via radical abstraction and radical combination reactions. This would increase the hydrogen content of the coal so that either, liquid fuels could be formed directly, or less hydrogen gas would be required during subsequent liquefaction and upgrading.

This concept has been investigated by several research groups. Most studies have involved co-pyrolysis in a hydrogen atmosphere with added catalysts (6-11). It has been found that higher conversions to oil are obtained using a hydrogen versus an inert atmosphere (7) and that molybdenum based catalysts can also improve liquid yields. In many instances it has been determined that although conversions for individual materials are high, when they are mixed together liquid yields are somewhat diminished (8). Rubber tires have been found to enhance coal liquefaction, presumably via hydrogen donation, while PS and PE are reported to enhance the hydrocracking of coal (9).

In this study co-conversion experiments were performed on single plastics, an Illinois No.6 coal and coal/plastic blends. After initial screening studies using a thermogravimetric analyzer (TGA), several pyrolysis/liquefaction environments were examined using stainless steel microreactors. Pyrolysis was conducted in nitrogen, steam and hydrogen environments, while liquefaction reactions used tetralin/H₂ conditions. Various reaction times and temperatures were investigated. No added catalysts were used in these experiments.

EXPERIMENTAL

Materials

Samples of PE, PS and PP were obtained from Aldrich Chemical Company. The coal sample (Illinois No. 6) was obtained from the Coal Research Center at Southern Illinois University at Carbondale. The coal was physically cleaned to remove mineral matter

via a combination of micronization and centrifugation in a solution of cesium chloride of 1.6 specific gravity. Ultimate analysis of the cleaned coal sample gave: 76.2% C, 5.02% H, 1.07% N, 2.79% S, 3.89% ash and 7.32% moisture. (All reported on a dry basis except moisture.)

Thermogravimetric Analysis

Initial screening experiments were performed on a Perkin-Elmer TGA7 using a sample weight of about 10mg. An inert gas flow of nitrogen was maintained throughout the heating period which was ramped from room temperature to 1000°C at 15°C per minute. Weight loss was measured continuously at a frequency of 0.2Hz. Pyrolysis profiles were presented as a function of weight loss versus temperature and also as a first derivative of weight loss versus temperature.

Microreactor Experiments

The microreactor apparatus used consisted of a 15 mL stainless steel tube type reactor sealed at one end but open to a three-way valve at the other. The other connections to the three-way valve incorporated a gas sampling device to acquire gas samples, a 2000 psi safety valve, a pressure transducer, and a quick-connect/disconnect assembly for easy gas charging. Typical co-conversion experiments used a 2g charge of coal, plastic or coal/plastic mixture. After the sample was loaded, air was eliminated from the system by repeatedly pressurizing then depressurizing with the desired gas (nitrogen or hydrogen). The microreactor was then immersed in a fluidized sand bath maintained at the desired reaction temperature. After completion of the reaction period the microreactor was cooled in a cold fluidized sand bath. (A cold water bath was found to cause the development of leaks in the microreactor set-up.) The microreactor was continuously shaken throughout the reaction period. When steam and tetralin were used, 2 mL of distilled water or tetralin were added to the microreactor respectively. A cold pressure of 500psig of hydrogen was used for the hydrolysis and liquefaction experiments. Conversions were measured via extraction of the products with tetrahydrofuran (THF) using soxhlet apparatus. The percentage conversion is given by the difference in weight between the original charge and the THF insoluble material, divided by the original charge weight.

RESULTS

Thermogravimetric Analysis of Co-pyrolysis

Initial examination of the behavior of a co-pyrolyzing system using the TGA suggested that there was significant interaction between the components of the system. This data has been examined in some detail and has been submitted for publication and therefore will receive only brief mention here. Generally it was found that characteristic pyrolysis parameters such as the temperature of weight loss onset, the temperature of maximum rate of weight loss, the temperature of final char formation and the temperature range of volatilization are all dramatically altered by the presence of another component in the system. For example, the presence of coal appears to retard the volatilization of both PP and PE such that the observed weight loss onset temperatures for the coal/plastic mixtures are higher than either the coal or the plastic. Also, the addition of PP and PE to coal appears to aid the conversion of the coal. Lower normalized chars yields are obtained when these plastics are co-pyrolyzed with the coal. In addition, these increased coal conversion are obtained at much lower temperatures than when the plastic is absent. These results point to an interaction between the coal and plastic as they both pyrolyze. Such interactions are necessary if our goal of liquefying coal using waste plastics is to be realized.

Microreactor studies

i) Conversion in Nitrogen:- Table 1 reports the conversions of single materials and their 1:1 blends obtained at various temperatures during a one hour standard reaction time. In general, conversions increase up to a temperature of 425°C where they remain constant until about 475°C after which they tend to decline. This can be attributed to the initial decomposition of the plastics into soluble materials at the lower temperatures, but then to the formation of char at higher temperatures. In general, the conversion data for the 1:1 blends in a nitrogen pyrolysis atmosphere is very close to that predicted by simply averaging the conversions of the individual components. This is an indication that the apparent synergisms observed in the TGA experiments do not transfer to confined microreactor tests.

In another two series of experiments the pyrolysis temperature was held constant at 425°C and 475°C respectively, but the reaction time varied from 5 minutes to 2 hours. It was found that in most cases maximum conversions were obtained after only 15 minutes. In general, longer reactions times did not improve the conversions and in some cases actually led to diminished conversions. This indicates a tendency towards char formation at longer reaction times. Small synergistic conversions for some coal/plastic blends were observed at the shorter reaction times. At longer reaction times this apparent synergism was lost.

ii) Conversion in Steam:- Table 2 reports conversions obtained at various temperatures in a steam atmosphere. Both 5 minute and one hour reaction times were investigated. In general, coal conversion of 25 to 30% was obtained which is similar to that obtained in nitrogen. The plastic conversions in a steam environment were somewhat lower than they were under nitrogen. Thus, the steam appears to retard plastic depolymerization. Some apparent synergistic conversion of the coal/plastic blends is observed especially for the coal/PP mixture. However, most of this synergism appears to result from the retardation of the plastic decomposition under steam. In general, the conversion values obtained for the blends in the steam atmosphere are similar to those obtained in nitrogen.

iii) Conversion in Hydrogen:- The conversions obtained using various temperatures with a 5 minutes and one hour reaction time in 500 psig (cold pressure) hydrogen are reported in Table 3. Somewhat surprisingly the conversions obtained for both the individual materials and the blends were similar to those obtained in nitrogen. Thus, the presence of hydrogen does not appear to enhance the conversion of these materials to soluble products.

iv) Conversion in Hydrogen/Tetralin:- Table 4 reports conversions obtained using 500 psig hydrogen and a 1:1 tetralin to charge ratio. Not surprisingly coal conversions are significantly higher in the liquefaction environment. However, the conversion of the individual plastics appears to be dramatically inhibited by these liquefaction conditions. Indeed, PP conversions as low as 14% were observed after 15 minutes at 425°C in the presence of tetralin and hydrogen gas. Under similar conditions in a nitrogen environment a PP conversion around 95-100% is observed. In some case the total conversions of the coal/plastic blends do not show that much improvement over those obtained in the other pyrolysis environments. However, other coal/plastic mixtures, especially those involving PP, do show higher conversions in the liquefaction environment compared to the other pyrolysis environments. Due to the low conversions of the individual plastics, the conversions of the coal/plastic blends often indicate significant synergistic conversion. Either short time high temperature or long time low temperature conditions appear to give the best results.

v) Product analysis:- Ultimate analysis was performed on some of the insoluble residues obtained from the microreactor experiments. Although the data is preliminary at this time it is clear that many of the insoluble residues from the co-pyrolysis and co-liquefaction experiments have very high volatile matter contents. For instance, a coal/PE blend reacted at 400°C in the liquefaction environment gave a conversion of 60% based on THF solubility. However, the residue was found to contain a 90% volatile yield when heated in the TGA. If we assume all the material soluble in THF is volatile, then distillation of this product would give a distillate yield of 95%. Comparison of elemental compositions showed that the residues derived from coal/plastic blends were depleted in sulfur but enhanced in hydrogen compared to the residues derived from the coal alone. This suggests that hydrogen was transferred from the plastic to the coal and helps to explain the high volatile matter contents of many of the insoluble residues.

SUMMARY AND CONCLUSIONS

Initial investigation of the co-pyrolysis behavior of coal with plastics using a TGA indicated that there were significant interactions between the coal and plastic as both degraded simultaneously. These interaction led to increased coals conversion at lower temperatures. Attempts to repeat these results using microreactors were only partially successful with much of the synergism that was observed during the TGA experiments apparently being lost when the larger scale and higher pressure microreactors were used. This discrepancy between the TGA and microreactor conversion data should not be that surprising since the TGA conversions are based on distillate yield whereas

microreactor conversions are based on solubility in THF. Indeed, many of the THF insoluble residues from the microreactors contain significant volatile matter contents which would have been reported as converted material in a TGA analysis.

In general, it was found that the conversion of pure plastics to liquid or gaseous products was almost complete during pyrolysis experiments but was significantly retarded in a liquefaction environment. On the other hand the highest conversions of coal and coal/plastic blends, especially coal/PP blends, were achieved under these liquefaction conditions. The majority of the conversion values obtained in a reactive pyrolysis environment such as steam or hydrogen, were very similar to those obtained in an inert nitrogen atmosphere. In some instances the presence of the steam or hydrogen gas appeared to hinder the formation of THF soluble material. Throughout the series of co-conversion systems examined in this study there was a general trend towards lower conversions with increasing process temperature and increased reaction time. This is attributed to char formation under these conditions. Although the results gathered so far are preliminary in nature, it can be appreciated that the use of waste plastics in coal liquefaction processes has great potential.

ACKNOWLEDGEMENTS

We would like to thank the following for support of this research: Illinois Clean Coal Institute (project No. 93-1/1.1B-2M), United States Department of Energy (grant No. DE-FC22-92PC92521), Office of Solid Waste Research at the University of Illinois, and the Materials Technology Center at SIUC.

REFERENCES

1. Farcasiu, M. PETC Review, 1991, p4-15.
2. Ainsworth, S.J. Chemical and Engineering News, August 31 1992, p34-55.
3. Reisch, M.S. Chemical and Engineering News, May 4 1992, p29-42.
4. Erwin, L. and L.H. Jr. Healy. Packaging and Solid Waste. Management Strategies. 1990, American Management Association, New York.
5. Hegberg, B.A., G.R. Brenniman, and W.H. Hallenbeck. Technologies for recycling post-consumer mixed plastics. 1991, University of Illinois.
6. Taghiei, M. M., Huggins, F.E. and Huffman, G.P. Am. Chem. Soc. Div. Fuel Chem. Prepr., 1993, 38(3), pp 810-815.
7. Liu, K., Jakab, E., McClennen, W.H. and Meuzelaar, H.L.C. Am. Chem. Soc. Div. Fuel Chem. Prepr., 1993, 38(3), pp 823-830.
8. Anderson, L.L and Tuntawiroon, W. Am. Chem. Soc. Div. Fuel Chem. Prepr., 1993, 38(3), pp 816-822.
9. Ibrahim, M.M. and Seehra, M.S. Am. Chem. Soc. Div. Fuel Chem. Prepr., 1993, 38(3), pp 841-847.
10. Orr, E.C., Tuntawiroon, W., Anderson, L.L. and Eyring, E.M. Am. Chem. Soc. Div. Fuel Chem. Prepr., 1994, 39(4), pp 1065-1072.
11. Hodek, W. Proc. Int'l. Conf. Coal Sci., 1991, Newcastle-Upon-Tyne, pp782-785.

TABLE 1.

Conversions obtained after 1 hour in a nitrogen atmosphere.

Temperature	Coal	PE	PP	PS	Coal/PE	Coal/PP	Coal/PS
350	21		35	97	62	13	
400	26	55	97	98	63	57	50
425	27	100	98	99	64	60	60
450	26	99	99	99	64	59	55
475	23	99	94	100	63	60	57
500	27	89	91		54	56	
525	31	85	85	83	55	60	57
550	23	82	79	84	56	54	52

Table 2.

Conversions obtained in a steam pyrolysis atmosphere

	5 minutes			60 minutes	
	425°C	475°C	525°C	425°C	475°C
Coal	24	30	25	26	18
PE	32	35	98	95	60
PP	70	82	79		70
PS				94	93
Coal/PE	35	50	57	64	60
Coal/PP	54	50	57	51	
Coal/PS				64	62

Table 3.

Conversions obtained in a hydrogen pyrolysis atmosphere

	5 minutes			60 minutes		
	425°C	475°C	525°C	425°C	475°C	525°C
Coal	27	25	20	20	25	24
PE	23	95		97	96	93
PP	26	99	95	96	87	87
Coal/PE	32	55	63	50	58	58
Coal/PP	66	58	60	63	57	58

Table 4.

Conversions obtained in a liquefaction environment.

	15 minutes			60 minutes		
	400°C	425°C	450°C	400°C	425°C	450°C
Coal	55	51	54	52	62	52
PE	45	47	79	42	48	70
PP	10	14	82	39	53	96
Coal/PE	60	40	60	44	62	
Coal/PP	61	62	84	79	71	73